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The Heat of Formation of Tetrafluoromethane[1]

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The purpose of this note is to report a preliminary value for the heat of the reaction

$$CH_4(g) + 4F_2(g) \longrightarrow CF_4(g) + 4HF(g) \quad (1)$$

and a value for the heat of formation of CF_4 derived therefrom.

The measurements were made by "burning" weighed samples of methane with fluorine in a flame at constant pressure. The reaction took place in a copper reaction vessel immersed in the water of an electrically-calibrated calorimeter of the type described by Dickinson,[2] which was used to measure the heat of the reaction.

The construction of the burner is shown schematically in Fig. 1. Helium gas entering through the annular space surrounding the methane inlet tube was intended to keep the methane–fluorine flame from resting on the end of this tube. In preliminary experiments it was found that without the flow of helium the reaction was incomplete, as shown by the deposition of carbon around the methane port. With the arrangement shown in Fig. 1 the deposition of carbon was negligible.

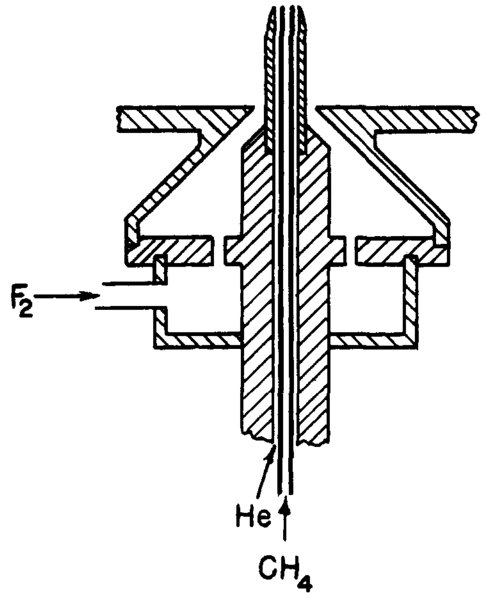

Fig. 1.—Schematic diagram of burner.

After leaving the reaction vessel the product gases passed through a helical monel tube, which served as a heat exchanger, before leaving the calorimeter. Hydrogen fluoride was removed from the fluorine before it entered the calorimeter by passing it over sodium fluoride maintained at Dry Ice temperature. Hydrogen fluoride formed in the reaction in the calorimeter was collected by means of a similar arrangement. The tetrafluoromethane formed was collected by condensation in a trap immersed in liquid nitrogen. The product gases were diluted with helium before entering the trap in order to reduce the partial pressure of the fluorine below its saturation pressure at the temperature of liquid nitrogen. Attempts to determine the amount of the reaction from the masses of HF and CF_4 formed were unsuccessful because of absorption of fluorine, or some of the impurities therein, by the sodium fluoride, and because of failure of the cold trap to retain all of the CF_4 passed into it. In the measurements reported the amount of reaction was determined by weighing the methane consumed.

The methane used was a purified sample which was analyzed by a mass spectrometer and found to contain the following amounts of impurities, expressed in mole per cent.: C_2H_6, 0.15; C_3H_8, 0.05; C_4H_{10}, 0.02; CO_2, 0.04; and N_2, 0.04. Impurities in the commercial fluorine used were determined by passing a measured amount of fluorine mixed with an equal volume of helium through a trap immersed in liquid nitrogen, weighing the condensate and analyzing it by means of a mass spectrometer. Similar analyses were made of the exhaust gases from the reaction vessel in each calorimetric experiment. Impurities found in the fluorine include CF_4, C_2F_6, C_3F_8, CO_2, water and air, together with small amounts of unidentified constituents. The total amount of impurities in the various tanks of fluorine ranged from near zero to about 4 mole per cent. The same impurities were found in the exhaust gases in any given experiment as in the fluorine used in that experiment, but usually in slightly different amounts. No fluorocarbons other than CF_4 were found in the exhaust gases unless they were also present in the fluorine used.

In calculating the results of the calorimetric experiments corrections were applied for the impurities in the methane, for reactions involving impurities in the fluorine, and for polymerization of hydrogen fluoride formed in the reaction. The correction for reactions involving impurities in the fluorine were calculated on the basis of the differences between the amounts of such impurities introduced with the fluorine, and the amounts collected in the products of the reaction. This correction is subject to considerable uncertainty because of possible errors of analysis, including errors resulting from the fact that some impurities were not identified, and because of uncertainty in estimated values for the heats of reaction of the impurities. Fortunately, the values found for the correction are relatively small, ranging from −0.5 to +1.0 kcal. per mole of CH_4 reacted. The correction for polymerization of hydrogen fluoride was calculated on the basis of P–V–T data by Long, Hildebrand and Morrell,[3] and was found to be about +2.0 kcal./mole of CH_4 under the conditions of the experiments (32° and a partial pressure of HF of about 170 mm. of mercury). The heat of formation of CF_4 was calculated from the measured heats of fluorination of methane (reaction 1), using the values $\Delta H_f = -17.94$ kcal./mole for the heat of formation of methane[4] at 32°, and $\Delta H_f = -64.2$ kcal./mole for the heat of formation of hydrogen fluoride.[5]

The results obtained, referred to a temperature of 32°, are tabulated.

Experiments 1 and 2 which gave the respective values −219.4 and −215.8 kcal. per mole for ΔH_f were rejected because of a leak in the methane line which was discovered after experiment 2.

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[1] This paper is based on research sponsored by the Ordnance Corps, U. S. Department of the Army.

[2] H. C. Dickinson, *Bull. Bur. Standard*, **11**, 189 (1914); Sci. Paper 230.

[3] R. W. Long, J. H. Hildebrand and W. E. Morrell, THIS JOURNAL, **65**, 182 (1943); see also R. L. Jarry and W. Davis, Jr., *J. Phys. Chem.*, **57**, 600 (1953).

[4] NBS Circular 461, Table 1w, 334 (1947).

[5] NBS Circular 500, Table 9-1, 19 (1952).

Experiment	Cor. temp. rise, °C.	Mass methane, g.	Obs. ΔH for reaction 1, kcal./mole CH_4	Corrections for Impurities in fluorine, kcal./mole CH_4	Corrections for Polymerization of HF, kcal./mole CH_4	Cor. ΔH for reaction 1, kcal./mole CH_4	ΔH_f for CF_4, kcal./mole
3	3.0153	0.37209	−461.0	−0.5	+1.8	−459.7	−220.8
4	3.1345	.38766	−460.0	+1.0	+2.0	−457.0	−218.1
5	3.1018	.38098	−463.2	0.0	+2.0	−461.2	−222.3
Mean						−459.3	−220.4

It is believed that the mean result is good to about ±2%, but it would be desirable to repeat the measurements using purified fluorine. A new determination of the heat of formation of hydrogen fluoride also would be desirable.

Data reported elsewhere on the heat of formation of CF_4 include the following values in kcal. per mole

ΔH_f	Method	Authors
−162 ± 2	Reaction of F_2 with charcoal	von Wartenberg and Schutte[6]
−231 ± 3	Reaction of CF_4 with K	von Wartenberg[7]
−218 ± 2	Reaction of CF_4 with K	Kirkbride and Davidson[8]
−213	Explosion and hydrogenation of C_2F_4	Duus[9]
−218	Combustion of teflon-oil mixtures	Scott, Good and Waddington[10]

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(6) H. von Wartenberg and R. Schutte, *Z. anorg. Chem.*, **211**, 222 (1933).

(7) H. von Wartenberg, *ibid.*, **258**, 356 (1949).

(8) F. W. Kirkbride and F. G. Davidson, *Nature*, **174**, 79 (1954).

(9) H. C. Duus, E. I. du Pont de Nemours and Co., Wilmington, Del., presented at the meeting of American Chemical Society in New York on September 15, 1954.

(10) D. W. Scott, W. D. Good, and Guy Waddington, THIS JOURNAL, **77**, 245 (1955).

NATIONAL BUREAU OF STANDARDS
WASHINGTON 25, D. C.

Heat of Formation of Tetrafluoromethane from Combustion Calorimetry of Polytetrafluoroethylene[1]

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When polytetrafluoroethylene (Teflon) reacts with oxygen in a calorimetric bomb that initially contains some water, the net reaction may be represented by the equation

$$C_2F_4(\text{solid polymer}) + O_2 + (2 - 2x + 4n - 4nx)H_2O = (2 - x)CO_2 + xCF_4 + (4 - 4x)HF\cdot nH_2O \quad \text{(I)}$$

In equation 1, x is the fraction of the fluorine that appears in the products as tetrafluoromethane. When the charge in the combustion bomb is pure Teflon, x is about 0.8. When the charge is a mixture of Teflon and a hydrocarbon oil, values of x anywhere in the range 0 to 0.8 may be obtained by suitably varying the relative amounts of Teflon and oil. This circumstance made possible a simple determination of the heats of hydrolysis and formation of tetrafluoromethane.

Combustion experiments with Teflon and with Teflon–oil mixtures were made with a rotating-bomb calorimeter.[2] Errors in the experimental determinations and in reduction of the data to standard states were minimized by the use of comparative experiments in which hydrofluoric acid solution was initially added to the bomb and the charge was a mixture of benzoic acid and oil or of benzoic acid and succinic acid. The comparative experiments were so designed that the energy evolved and the amounts of final products (except CF_4) were essentially the same in the combustion and comparative experiments.

The following table presents the values obtained for the heat of reaction 1 (n = 10) as a function of x.

x	0.0285	0.0564	0.1178	0.2577	0.2678	0.3645
$\Delta H^\circ_{298.16}$, kcal. monomole^{-1}	−157.7 ±1.8	−157.5 ±1.3	−156.2 ±0.9	−149.6 ±0.6	−149.3 ±0.5	−145.2 ±0.5
x	0.5388	0.5702	0.7972	0.8104	0.8162	
$\Delta H^\circ_{298.16}$, kcal. monomole^{-1}	−137.9 ±0.2	−136.9 ±0.2	−127.1 ±0.1	−126.6 ±0.1	−126.5 ±0.1	

The estimated uncertainty is greater at smaller values of x because more of the heat measured calorimetrically came from combustion of the admixed oil and less from the Teflon. The experimental values are represented within the estimated uncertainty by the equation

$$\Delta H^\circ_{298.16} = -160.3_4 + 41.5_5x \text{ kcal. monomole}^{-1}$$

For the limits of x equal to 0 and 1

$$C_2F_4(\text{solid polymer}) + O_2(g) + 42H_2O(l) = 2CO_2(g) + 4HF\cdot 10H_2O(l) \quad \text{(II)}$$
$$\Delta H^\circ_{298.16} = -160.3 \pm 0.9 \text{ kcal. monomole}^{-1}$$

$$C_2F_4(\text{solid polymer}) + O_2(g) = CO_2(g) + CF_4(g) \quad \text{(III)}$$
$$\Delta H^\circ_{98.16} = -118.8 \pm 0.5 \text{ kcal. monomole}^{-1}$$

The difference of equations II and III gives the heat of hydrolysis of tetrafluoromethane.

$$CF_4(g) + 42H_2O(l) = CO_2(g) + 4HF\cdot 10H_2O(l)$$
$$\Delta H^\circ_{298.16} = -41.5 \pm 1.0 \text{ kcal. mole}^{-1}$$

The value of the heat of hydrolysis is independent of the particular thermodynamic state, *i.e.*, degree of crystallinity, of the Teflon sample, because of cancellation that occurs when equation III is substracted from equation II.

Use of the values −94.0518, −68.3174 and −75.605 kcal. mole^{-1} for the standard heats of formation of $CO_2(g)$, $H_2O(l)$ and HF (solution in $10H_2O$) at 298.16°K.[3] leads to the derived value for the heat of formation of tetrafluoromethane.

$$C(\text{graphite}) + 2F_2(g) = CF_4(g)$$
$$\Delta H^\circ_{298.16} = -218.3 \text{ kcal. mole}^{-1}$$

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(1) (a) This research was supported by the United States Air Force, through the Office of Scientific Research of the Air Research and Development Command. It is part of a broad program of combustion calorimetry of solid and liquid organic fluorine compounds. (b) For references to early and contemporary heat of formation studies on tetrafluoromethane, see R. S. Jessup, R. E. McCosky and R. A. Nelson, THIS JOURNAL, **77**, 244 (1955).

(2) Similar to that described by W. N. Hubbard, C. Katz and G. Waddington, *J. Phys. Chem.*, **58**, 142 (1954).

(3) "Selected Values of Chemical Thermodynamic Properties," Circular 500 of the National Bureau of Standards, Washington, D. C., 1952; Series 1, Tables 2-1, 9-2 and 23-2.